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Formation of nascent char structure during the fast pyrolysis of mallee wood and low-rank coals

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HIGHLIGHTS

- This study examines the structural changes from coal/biomass to nascent char during pyrolysis.
- Heating coal rapidly to 600 °C causes insignificant changes to the aromatic rings and cross-links.
- Sub-bituminous coal behaves very differently from brown coal and wood during initial pyrolysis.

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ABSTRACT

The structural evolution of nascent chars during the fast pyrolysis of a wood and two low-rank coals was investigated in this study. Western Australian Collie sub-bituminous coal, Victorian Loy Yang brown coal and Western Australian mallee wood were pyrolysed in a wire-mesh reactor that is capable of providing rapid heating rates (up to 5000 K s^{-1}) and accurate holding time (in increments of 10 ms) at peak temperature. FT-Raman spectroscopy was used to characterise the key structural features of raw fuels and nascent chars. The combined use of a wire-mesh reactor and a FT-Raman spectroscopy has given insights into the structural transformation from coal/biomass to nascent chars. There were insignificant changes in the aromatic ring systems of two coals during the initial fast heating from room temperature to 600 °C. During holding at 600 °C, the changes that occurred in ring systems for the three fuels were different. Mallee wood and Loy Yang coal underwent more changes than Collie coal. In addition, mallee wood had ring condensation during holding at 600 °C up to 30 s. However, little growth in large aromatic rings of two coals was observed during holding at 600 °C up to 50 s.

1. Introduction

Gasification converts solid fuels into clean syngas and is the core of many low-emission energy technologies [1]. As the char gasification rate controls the overall gasification rate [2], effort has been made to evaluate the possible factors influencing the char reactivity [2–4]. Among many important factors, the structural evolution of char has been shown [4–17] to be a significant aspect that affect the changes in coal [4–7] or biomass [8–11] char reactivity and the behaviour of catalysts [13–15].

The formation of char is complicated. Several structural changes could take place in the initial transition from coal to char with the concurrent release of volatiles. For example, while large aromatic and heteroaromatic ring systems (e.g. with more than 4 or 5 fused benzene rings) dominate in the char structure, they exist in low-rank coals at relatively low concentrations [18,19]. The long-chain aliphatics in a low-rank coal are almost absent in its chars formed at 600 °C and higher [20]. Many O-containing functional groups (e.g. carboxylic acids) in abundance in a low-rank coal will also be decomposed and released as gases [20] during the initial process to form a char. Some recent studies in our group focused on the changes in relatively "old" char structure during pyrolysis/gasification in fluidised bed for biomass [8–11] and low-rank coal [12–14,16,17]. However, there is a lack of experimental data on the detailed structural features of the newly formed (nascent) char. The time scale for the conversion of coal to char is very short: the evolution of tar is completed as soon as the coal particles are heated up to 600 °C at 1000 K s^{-1} [21,22]. Very few reactors are capable of providing a well-controlled heating rate and a high resolution of holding time. A wire-mesh reactor [21–23] is one such reactor due to its well-known ability to control linear heating rate over a wide range from 0.1 to 5000 K s^{-1} and to provide holding time in increments of 10 ms.

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Volatile–char interactions can drastically change the pathway of char structural evolution [3]. A wire-mesh reactor has the special advantage in that volatiles, once released from the parent pyrolysing coal/char particles, are swept away and will have minimal inter-particle interactions with the char particles. Therefore, the wire-mesh reactor provides a means to investigate the structural formation of nascent char in the absence of the influence of volatile–char interactions.

A quantitative method to describe the char chemical structural features is a necessity to trace the development of char structure during pyrolysis. Our recent studies have shown that FT-Raman spectroscopy combined with spectral deconvolution is a powerful technique to semi-quantify the structural features of chars produced from the pyrolysis/gasification of biomass [8–11] and coal [12–14,16,17]. The FT-Raman spectra of coal/char over the range between 800 and 1800 cm^{-1} were deconvoluted into 10 bands [12]. The overall changes in the aromatic structures, oxygen-containing functional groups and cross-links can be investigated.

The purpose of this study is to characterise the chemical structural features of nascent chars during the pyrolysis of Loy Yang brown coal, Collie sub-bituminous coal and Western Australian mallee wood. By using FT-Raman spectroscopy on the analyse of the chars prepared in a wire-mesh reactor, our results reveal some details about the structural information of nascent char, especially the changes in char structure during the initial release of tar at <600 °C with 1000 K s^{-1} heating rate and the changes after further holding at 600 °C with the holding time up to 50 s. All experiments were carried out at atmospheric pressure.

2. Experimental

2.1. Samples preparation

Collie sub-bituminous coal from Western Australia, Loy Yang brown coal from Victoria and mallee wood from Western Australia were used. The preparation procedure of Collie coal was the same as that for Loy Yang coal [24]. Briefly, "as mined" coal with particle sizes mainly around 10–20 cm was obtained and dried at ambient temperature. The air-dried raw coal was pulverised and screened to the particle size range of 106–150 μm. The preparation of mallee wood was described elsewhere [25], the wood with particle size range of 180–400 μm was chosen. As the mallee wood particles were long and thin, the particles were cut into circular-like pieces by hand to obtain a better particle distribution on the sample holder. The proximate and ultimate analyses of the three fuels are shown in Table 1.

2.2. Pyrolysis

The pyrolysis of the three fuels was carried out using a wire-mesh reactor at a fast heating rate of 1000 K s^{-1}. The details of the wire-mesh reactor and the operation procedure can be found elsewhere [23,24]. Briefly, a small amount of coal or biomass (typically less than 10 mg) was sandwiched between two layers of mesh made from grade 316 stainless steel with an aperture of 45 μm. The mesh was stretched between two electrodes for heating samples with an alternating current. During the heating of the particles, a stream of ultra-high purity helium passed through the mesh vertically at the flow rate of 0.1 m s^{-1} (measured under ambient conditions). With the contribution of the cooling carrier gas (helium), volatiles were quenched and removed out of char immediately after evolution from the samples to minimise the volatile–char interactions.

The temperature of sample was detected by two pairs of chromel/alumel alloy wires. One pair was inserted at the centre of the area containing the coal particles and the other was inserted at around 1 mm from the edge. The average of these two temperatures was used as a feedback for controlling the mesh temperature with a PID control system. The holding time can be pre-set and controlled at 10 ms increments. The empty stainless steel sample holder was preheated to the target temperatures to prevent further weight loss in pyrolysis experiments. A balance with precision of 0.01 mg was used for all weight measurement. Char yield was determined by the difference in the weight of the loaded sample holder before and after an experiment. In addition, all the char in a single experiment was collected and directly mixed with KBr for Raman analysis.

2.3. Raman spectroscopy for char characterisation

The FT-Raman spectra of fuels and chars were acquired by using a Perkin–Elmer Spectrum GX FT-Raman spectrometer. The fuel/char sample was mixed, diluted and ground with spectroscopic grade potassium bromide (KBr) that was used as a heat dissipating agent [12]. The selection of coal/char concentration in KBr will be discussed in Section 3.3.1. The Raman spectra in the range between 800 and 1800 cm^{-1} were deconvoluted into 10 Gaussian bands. The assignment of 10 bands was summarised in our previous study [12]. An example of Raman spectrum with 10 bands deconvolution is shown in Fig. 1. The total Raman area and Raman band ratios were used to characterise the fuel/char structural features in this study.

3. Results and discussion

3.1. Char yields of three fuels during initial pyrolysis

Fig. 2 shows the changes in char yield as a function of holding time during the pyrolysis of Loy Yang brown coal, Collie

Table 1
Properties of three fuels [10,16,26].

	Proximate analysis (wt%)		Ultimate analysis (wt%)				
	Ash[a]	Volatile matter[b]	C[b]	H[b]	N[b]	S[b]	O[b,c]
Mallee wood	0.9	81.6	48.2	6.1	0.2	0.0	45.5
Loy Yang coal	1.1	52.2	70.4	5.4	0.6	0.3	23.2
Collie coal	5.7	38.8	75.7	4.5	1.4	0.5	17.9

[a] Dry basis.
[b] Dry and ash-free basis.
[c] By difference.

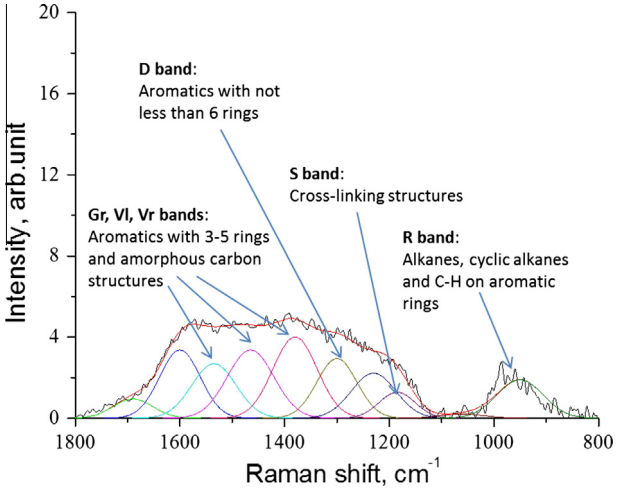

Fig. 1. Deconvolution of a Raman spectrum of Loy Yang char pyrolysed at 600 °C with 0 s holding. (Redrawn using new data based on that in [12], Copyright (2006), with permission from Elsevier).